

# Hexavalent Chromium: Use, Toxicology and Restrictions

Todd\_MacFadden@uml.edu

Toxics Use Reduction Institute

University of Massachusetts Lowell

# What is Chromium?

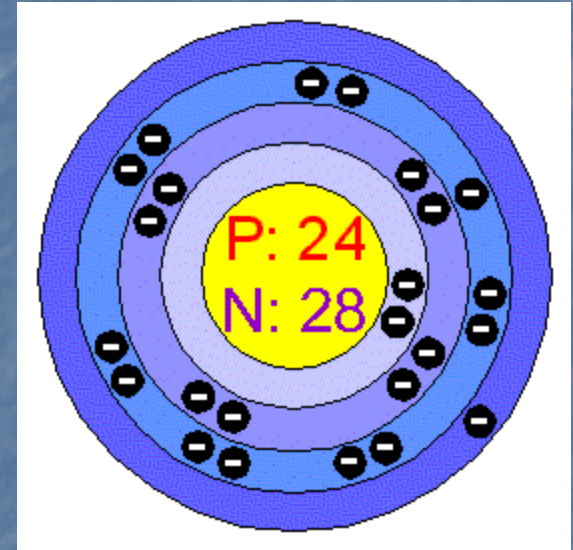
- Naturally occurring metallic element found in rocks, soil, plants and volcanic dust
- Exists primarily in mineral form, chromite,  $\text{FeCr}_2\text{O}_4$
- Chromite is the main constituent in chrome ore, and the only commercial source of Cr

1																	2
H																	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110								
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun								
58	59	60	61	62	63	64	65	66	67	68	69	70	71				
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
90	91	92	93	94	95	96	97	98	99	100	101	102	103				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				



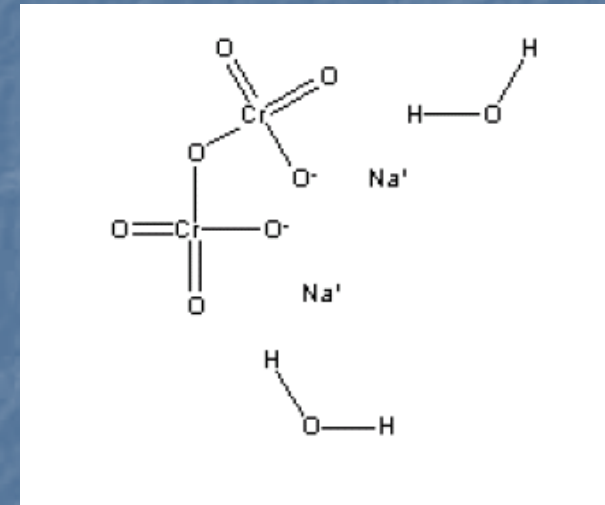
# Exists in several oxidation (valence) states

- Inorganic
  - Divalent ( $\text{Cr}^{+2}$ ) (uncommon)
  - Trivalent ( $\text{Cr}^{+3}$ )
  - Hexavalent ( $\text{Cr}^{+6}$ )
- Organic
- Elemental (Metallic ( $\text{Cr}^0$ ))

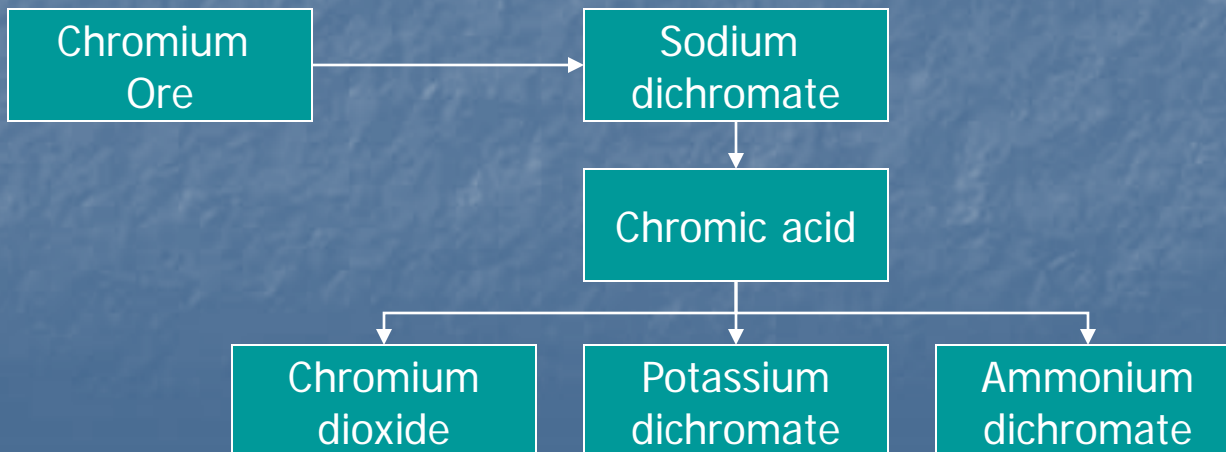


# Starting place for all chromium products is Cr+6

- Sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) is the starting place
- Chromic acid ( $\text{CrO}_3$ ) and sodium dichromate are the building blocks of all chromium chemicals used commercially



Sodium dichromate



# Industrial Uses of Cr

## ■ Metallic ( $\text{Cr}^0$ )

- Metal Cr
- Does not occur naturally
- Used for making steel (alloying agent)
- Chrome plating



## ■ Trivalent ( $\text{Cr}^{+3}$ )

- Most stable form
- Used in leather tanning, dyes, paint pigments, brick lining in furnaces



## ■ Hexavalent ( $\text{Cr}^{+6}$ )

- Occurs in a range of compounds
- Used in Chrome plating ( $\text{CrO}_3$ )
- Wood preserving
- Conversion coatings



# Properties of Different States

## ■ Metallic ( $\text{Cr}^0$ )

- Does not occur naturally
- Not toxic
- Metallic structure (body centered cubic) provides excellent wear resistance, and also means the Cr is bound in the metal matrix

## ■ Trivalent ( $\text{Cr}^{+3}$ )

- Insoluble in water
- Essential micro-nutrient (helps convert sugar, protein, & fat)
- Low toxicity – unless it enters a cell, then it can damage DNA

## ■ Hexavalent ( $\text{Cr}^{+6}$ )

- Soluble, readily absorbed
- Structurally similar to phosphate (“Trojan horse”)
- Converted to V-IV-III in cells
- Highly toxic

# Chromium in the environment

- Cr enters the air, water and soil in the +3 and +6 forms
- In air, Cr (+3 and +6) compounds exist as fine dust that settles (rain or snow help remove Cr)
- Strongly binds to soil, which can prevent it from reaching groundwater
- Does not bioaccumulate in fish



# Toxicological Responses to Cr+6

## Acute Responses:

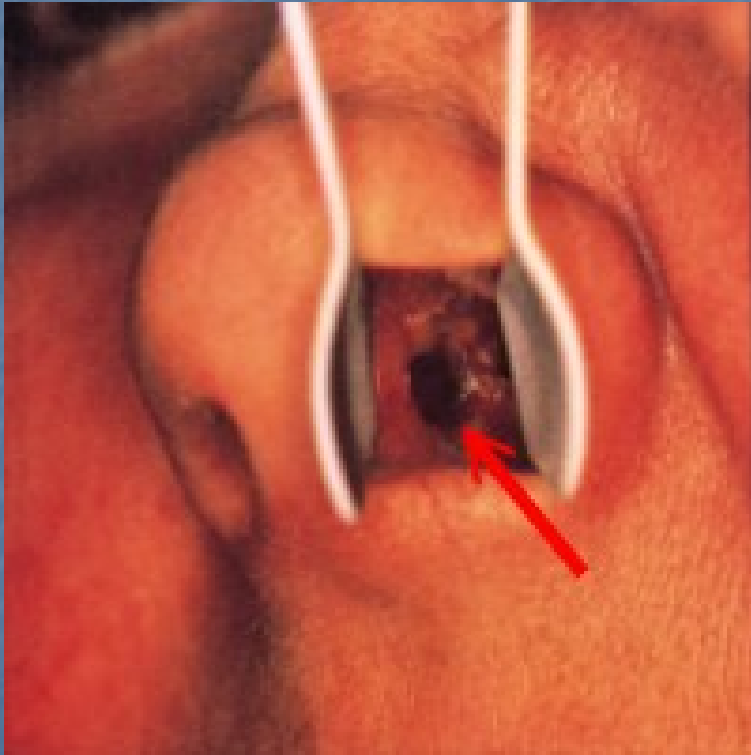
- Ulceration of nasal septum
- Allergic dermatitis (can be very severe)
- Asthma
- Permanent eye damage

## Chronic Responses:

- Lung cancer
- Cell injury: interferes with cellular respiration
- Ingestion can cause stomach, liver, kidney damage
- Teratogenic: probable, little data



# Acute responses to Cr+6



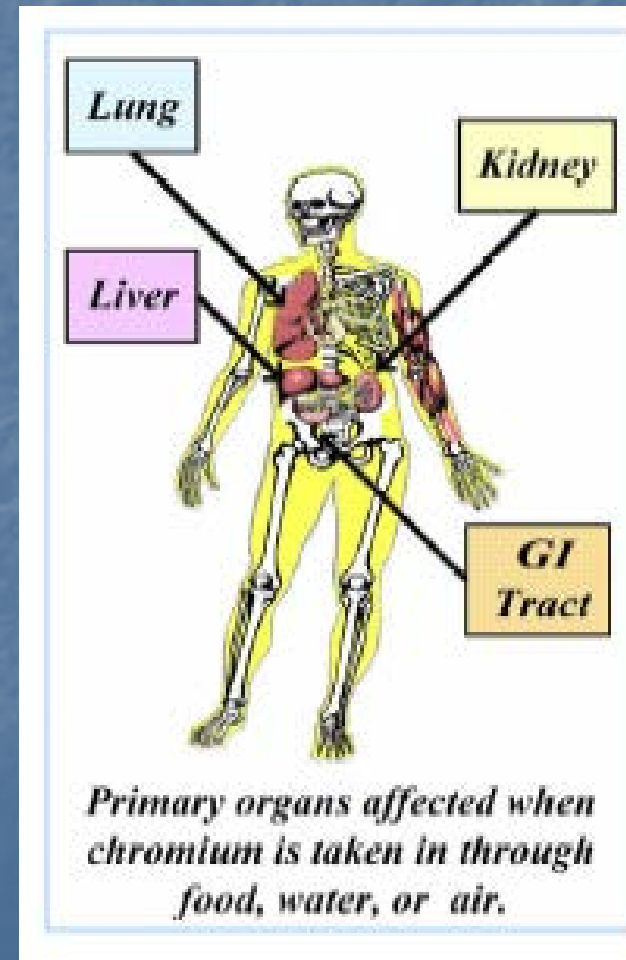
Perforated nasal septum



Severe dermatitis

# Chronic Responses to Cr+6

- Human carcinogen when inhaled
- Not cancer-causing when ingested
  - But damage to the GI tract, kidneys and liver may still result, particularly when large doses are ingested



# Erin Brockovich Factor

- PG&E used Cr(VI) for anti-corrosion
- Private wells contaminated – health effects of neighboring citizens observed
- Controversial – health risks through drinking water inconclusive
- \$333m settlement – likely to avoid further controversy and prolonged trial
- 1990 EPA rule banned Cr+6 in cooling towers and HVAC systems
- Non-chromate substitutes (molybdate salts and organic compounds) have largely replaced Cr compounds in anti-corrosion



# Regulation of Cr (VI)

- Primary contaminant in 1/2 of Superfund sites
- CalEPA – Toxicity review committee study of drinking water (2001) inconclusive
- Federal MCL for drinking water is 100 ppb
- Greatest proven threat to human health is inhalation exposure – therefore, it is primarily an occupational exposure issue

# Inhalation Exposure to Cr(VI)

Sources of Cr emissions:

- Oil and coal combustion (mostly Cr+3)
- Cement plants
- Chrome plating production
  - Avg conc: 10-30  $\mu\text{g}/\text{m}^3$  with ventilation
  - 120  $\mu\text{g}/\text{m}^3$  w/o ventilation
- Stainless steel production and welding
  - 1500  $\mu\text{g}/\text{m}^3$

(PEL: 100  $\mu\text{g}/\text{m}^3$ , REL is 1  $\mu\text{g}/\text{m}^3$ )





# European Union Directives

## End of Life Vehicle (ELV)

### (Directive 2000/53/EC)

PURPOSE: prevent waste from the recovery, reuse and recycling of vehicles

- Covers 3 and 4 wheel vehicles
- Eliminates four metals that make recycling difficult for vehicles marketed in Europe starting July 2003 (Model Year 2005)





# Hex Chrome Under ELV

- Total limit @ 2.0 grams/vehicle for Cr+6 for corrosion protection purposes only
  - Starting July 1, 2003 (automobile Model Year 2005)
  - Annex II exemptions allow 2 g hex chrome used in Corrosion Preventative Coatings until July 1, 2007
  - Limited thereafter to 0.1% (w/w) per homogenous material **NOT** *intentionally introduced*
- Currently there is no standard test method

Most OEMs banning  
Cr+6 completely



# Hex Chrome Under ELV

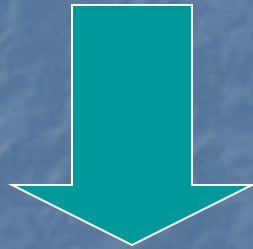
- Applies to chromate conversion coating for zinc and zinc alloy parts
  - Deliberately leave Cr+6 on the parts
  - Fasteners, tubing, brackets, etc. (1000s of parts)
  - Most common: yellow chromate
- Not affected:
  - Chrome plating = metallic chrome (0-valence chrome left on part)
  - Functional ("hard") chrome and decorative plating are NOT covered under this directive





# Hex Chrome Under ELV

- To do business in Europe, automakers must follow the ELV directive.
- Impossible to have one spec for Europe and another for the rest of the world



one universal specification is required

Hex-free is still  
in its infancy

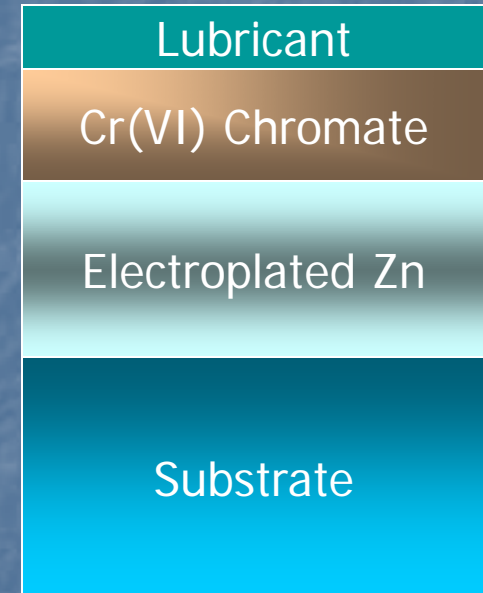


# Chromate Conversion Coatings

## COATING FEATURES

- Protection of sacrificial zinc (or zinc alloy) layer
- Excellent corrosion resistance
- Friction properties – organic coating adhere well
- Self-healing
- Wide range of colors possible (clear, blue-bright, iridescent, golden yellow, olive drab, matte black and bronze)
- Solderability
- Constant conductivity

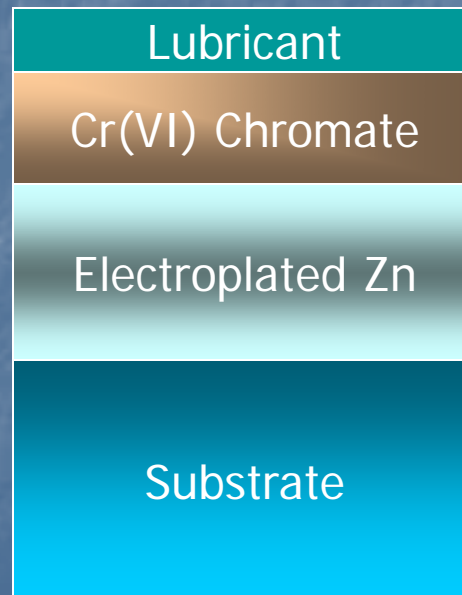
Traditional Cr (VI)  
Coating System



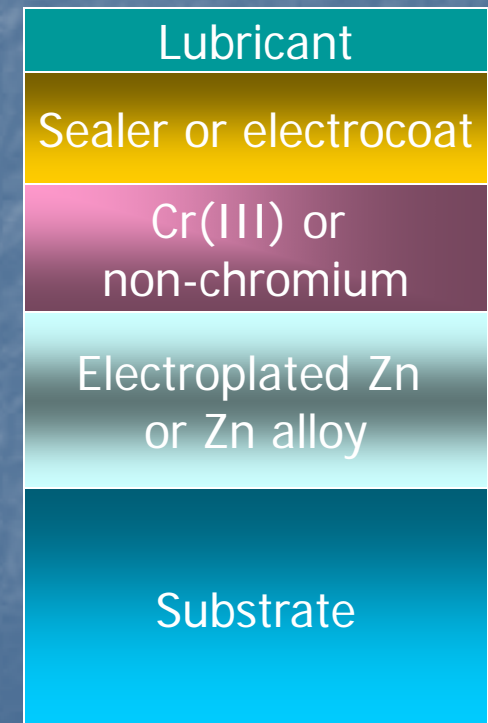
# Alternative Systems

- Lots of alternative coatings
- But no drop in substitute
- Cost will be higher
- Performance not equivalent to Cr+6

Traditional Cr (VI)  
Coating System



ELV Compliant  
Coating System





# Hex-free alternatives

## 1. Trivalent Chromate



- Most commercially acceptable alternative at lowest cost
- Suitable or superior corrosion resistance



- Not self-healing
- Growing realization all chromate to be phased out in time

## 2. Non-Chromium Passivations

(organic polymer films, inorganic salts, oxides, organometallics)



- Non-chromate



- Individual adoption seems unlikely
- Cost
- Similar corrosion resistance as Cr+6 not possible yet



# Conclusions

- Europe is moving
- Japan is trying to get ahead
- US recognizes the inevitable
- OEMs are passing on requirements to suppliers
- Suppliers that can meet those requirements will be in a good competitive position
- However, until customers specifically ask for them, non-chromate coatings may not be profitable

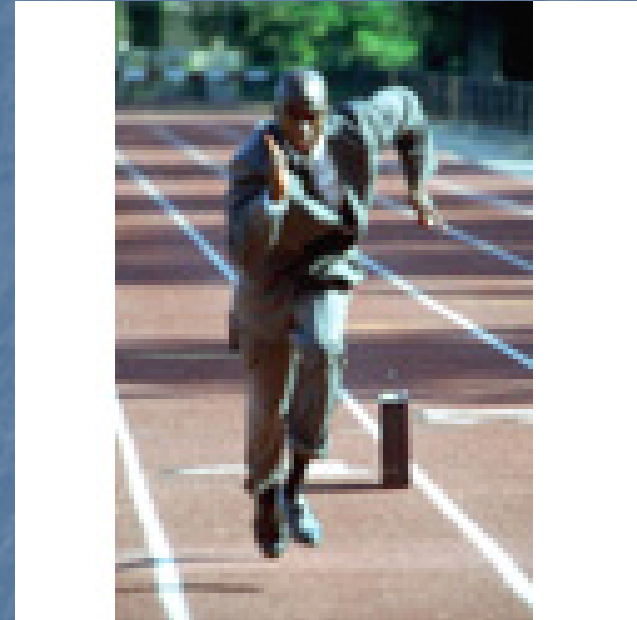


# What you can do

1. Stay informed



2. Get involved



**TURI's Metal Finishing Supply Chain Forum**

**[www.turi.org](http://www.turi.org)**

# Bibliography

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You the guy who just made a seven-coordinate compound of chromium III...?

Well we've got a MESSAGE for ya...

Chromium III doesn't LIKE being seven-coordinate ...



LATE THAT NIGHT, PROFESSOR ROBINSON'S LABORATORY WAS OVERRUN BY HOSTILE ELEMENTS.

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